Real-Time Needs for Beryllium Particle Detection

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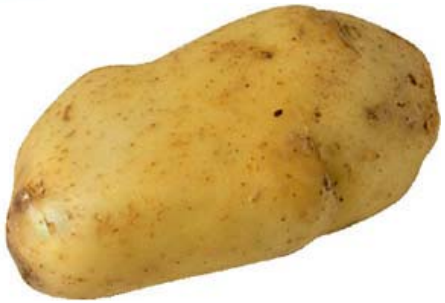
Overview

- Beryllium Uses (courtesy M. Hoover)
- The need identified
  - Overview of occupational exposure limits and current trends
  - Impact/cost of DOE Beryllium Rule
  - Recent developments within DOD
  - NIOSH NORA
- The need defined
  - What is available today
  - Benefits of direct-reading instrument
- What Has Been Tried So Far
  - Efforts up to 2002
  - Be Advanced Technology Assessment Team
  - Efforts Since 2002
- What We Need to Go Forward
  - Technology
  - Funding
- What Will Drive Further Progress?

(Source: ATSDR web site, http://www.atsdr.cdc.gov)

Beryllium is Found in ...



(aggie-horticulture.tamu.edu)

- Foodstuffs (μg per kg fresh weight – ATSDR 2002)
  - Milk (0.2)
  - Potatoes (59)
  - Crisp bread (112)
  - Kidney beans (2200)
- Soils (up to 15,000 μg/kg – USGS)
- Coal (0.2% - ATSDR 2002)
- Orchard Leaves (26 μg/kg – ATSDR 2002)
- Cigarettes (up to 0.74 μg/cigarette – ATSDR 2002)
- Minerals such as bertrandite, beryl, aquamarine, emerald

Beryllium Properties

- Lightweight
- High melting point (1287°C)
- Thermal conductivity
- Moderator
- Neutron reflector
- Relatively transparent to X-Rays
  - Used in windows for nondestructive analytical equipment
  - Techniques like point-and-shoot XRF not viable for Be detection

Uses for Be Products (20% - 100%)

- Satellites and spacecraft
- Guidance systems (military and commercial)
- Brake parts (automotive, aircraft)
- Nuclear weapons (neutron reflector)
- X-Ray windows
- Optical instruments
- High-end audio
- Sports equipment

(Source:Fermilab Web site, http://www-esh.fnal.gov)

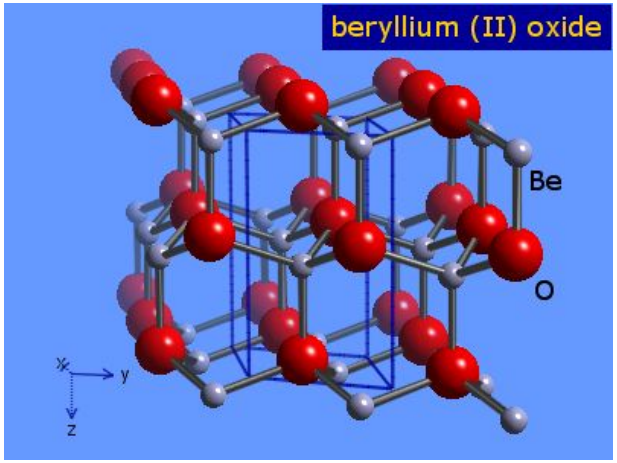
Beryllium Alloys

(CuBe at Brush-Wellman Elmore, OH, plant, http://www.brushelmore.com)

- Copper-beryllium (CuBe)
  - Resistant to metal fatigue failure
  - Resistant to corrosion
  - Rotary-dial telephone springs
  - Non-sparking tools
- Aluminum-beryllium (AlBeMet® - Brush-Wellman)
  - Resistant to corrosion
- Nickel-beryllium
- Uses for alloys:
  - Fire control sprinkler heads
  - Aircraft landing gear bushings
  - Current-carrying springs
  - Electromagnetic shielding

Beryllium Oxide

- Semiconductor parts
- Integrated circuits
- Good thermal conductivity
- Good electrical insulator
- Nuclear reactors
  - Moderator
  - Neutron reflector



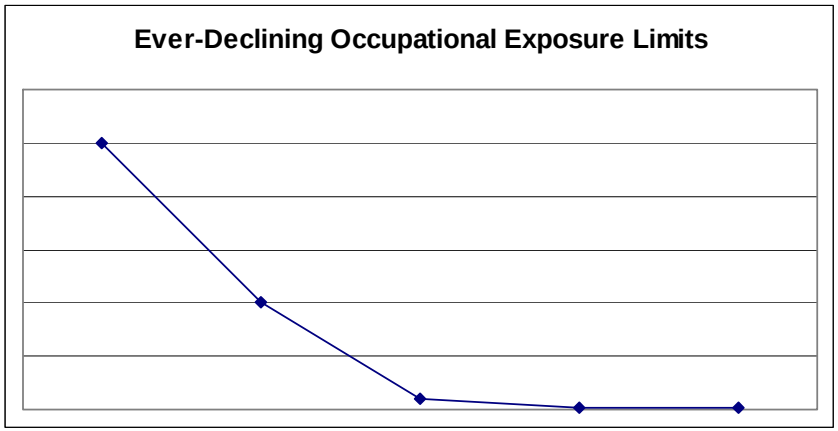
(Source: WebElements™, http://www.webelements.com Used with permission)

Occupational Exposure Limits

- ACGIH® Threshold Limit Value (TLV®) and OSHA Permissible Exposure Limit (PEL)
  - ACGIH® TLV® and OSHA PEL: 2 μg/m^3 (8-hour time-weighted average or TWA)
  - Same limit in Austria, Spain, France, Sweden, U.K., and Ontario
    - Denmark: 1 μg/m^3
  - Originally proposed in 1949 from Atomic Energy Commission studies
  - ACGIH® adopted TLV® in 1959 for beryllium; applied to "beryllium and compounds" in 1986
- Short-term exposure limits (STEL)
  - Maximum exposure for any 15-minute period
  - U.S.: 5 μg/m^3
  - Austria: 8 μg/m^3
  - Denmark, Hungary: 2 μg/m^3

(Source: Lawrence Livermore National Lab)

OEL Trends



(Illustration only)

- In 1990's, learned that the 2 μg/m^3 PEL/TLV level is not necessarily protective
  - Incidences of sensitization and CBD at lower exposure levels
- ACGIH has proposed several new TLVs since 1999
  - Current proposal: TLV of 0.05 μg/m^3 and STEL of 0.2 μg/m^3 (pending since 2006)

OEL Trends (2)

- OSHA
  - Rulemaking has been in progress since 2002
  - Currently evaluating range of exposure limits (0.1 – 1.0 μg/m^3 air)
- State of California
  - 2006: exposure limit of 0.2 μg/m^3 (air), equal to DOE action level
- Quebec Province
  - 2006: exposure limit of 0.15 μg/m^3

Bottom line trend: lower OELs

- Potential challenge for any direct-reading instrument

It's like the game of limbo … How low can you go??? (picture from nyiboosterclub.org)

DOE "Beryllium Rule" (10CFR850)

- Effective January 7, 2000
- Response to exposure concerns in DOE nuclear facilities
- Action level of 0.2 $\mu g/m^3$ (air, 8-hr TWA)
- Housekeeping within Be areas: 3 $\mu g/100cm^2$ (surface)
- Release to non-Be area: 0.2 $\mu g/100cm^2$ (surface)
  - Based on lab capabilities at that time – not health-based
  - OSHA, ACGIH® do not have surface wipe action levels like DOE; however, Quebec (IRSST) also does surface wipe measurements
- Measurement uncertainty within $\pm$25% at action level

Impact of DOE Beryllium Rule

SUMMARY: The Department of Energy (DOE) is today publishing a final rule to establish a chronic beryllium disease prevention program (CBDPP) to reduce the number of workers currently exposed to beryllium in the course of their work at DOE facilities managed by DOE or its contractors, minimize the levels of, and potential for, exposure to beryllium, and establish medical surveillance requirements to ensure early detection of the disease. This program improves and codifies provisions of a temporary CBDPP established by DOE directive in 1997.

EFFECTIVE DATE: This rule is effective January 7, 2000.

(64 FR 68854, 12/8/1999)

- Establishment of "beryllium inventory"
- Action levels at one-tenth the OSHA PEL
- Surface wiping as well as air sampling
- Operational impacts
  - Delays in receiving analytical results
  - Costs from sampling and analysis (over $3 million/year at some sites)
- Result: need for "real-time" monitoring capabilities
  - Improved worker and public protection
  - Improved productivity
  - Reduced lab and operating costs

Recent Developments Within DoD

- In 2007, beryllium added to Emerging Contaminants List
  - Contaminants of emerging concern to DoD due, for example, to potential regulatory changes such as lower OEL's
- Two-part National Academy of Sciences study
  - Commissioned by U.S. Air Force
  - Essentially recommends approach similar to what DOE adopted in 10CFR850

Beryllium and NIOSH NORA

- NIOSH National Occupational Research Agenda (NORA)
  - Partnership between NIOSH and Brush-Wellman originated in 1998
    - Basic epidemiology, exposure characterization, risk factor research
    - Development of enhanced worker protection model
    - Evaluate effects of model on worker risks
    - Communicate results throughout beryllium-using community
  - Received one of two 2008 NORA Innovative Research Awards
  - Partnership ongoing

Why a Beryllium Direct-Reading Instrument (DRI)?

- Current detection methods are laboratory-based
  - Collect samples in field and take to laboratory
  - Digest samples into acid solution or extract into ammonium bifluoride solution
  - Analyze via spectroscopy (ICP-AES, ICP-MS, GFAA) or fluorescence
    - ICP-AES most common in U.S.
    - May not be sensitive enough for proposed ACGIH TLV (8-hour or STEL)
  - Delay factor of 24 hours (best) to >1 week
    - Costly for ongoing processing operations

A Be Field Analyzer Wish List

- The "black box" wish list:
  - Real-time air monitor and surface wipe analyzer (ideally the same device)
  - Reporting limits comparable to lab analysis
  - Avoid/minimize liquid waste
  - Portable (NOT just "transportable")
  - Easy to use and maintain
  - Cheap
- A beryllium DRI would be ideal (this is the DREAM conference, right?)

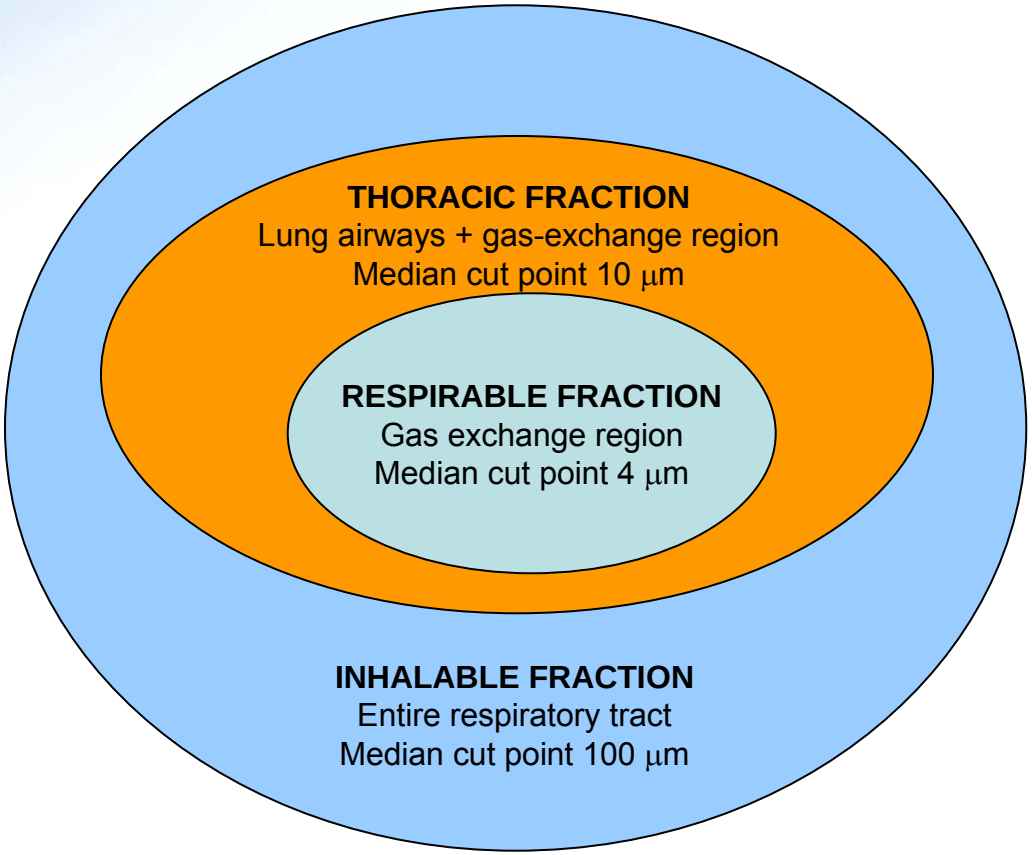
Potential DRI Benefits

- Could save millions per year in analytical costs for DOE alone
- Would improve worker protection by providing faster results
- Within DOE, most needed for surface sampling, but also needed for air monitoring
  - NAS study recommends housekeeping for which a surface DRI would be beneficial
- For aerosols, DRI could eliminate issue of wall deposits
  - Current air sampling uses closed face cassettes (CFC) of 25 or 37 mm
  - Some particulate collects on interior walls
  - Most labs only analyze filter catch
  - May underestimate Be to which workers are exposed

Potential DRI Issues

- Issues Common to Aerosols and Surfaces:
  - Validation
  - Cost and Portability
  - Detection Limits
  - Precision at low μg per sample levels (must be within ±25% of 0.2 μg per sample for DOE Beryllium Rule)
  - New technologies may need to be developed
  - DRI for both aerosols and surfaces may not be possible

DRI Issues (2) – Size-Selective Sampling



- ACGIH® NIC proposes inhalable fraction
  - Current U.S. practice does not follow any of the ISO sampling conventions
  - Would require larger air volume
  - Would shift focus away from fine (0-4 μm) particulate
- Aerosol DRI would need to address size-selective sampling requirements

DRI Issues (3) – Surface Sampling

- Nature of surfaces being wiped
  - Dimensions, porosity, roughness
- Amount of particulate (Be and otherwise) on surface
- Oils, greases, other potential interferences

Early Efforts, 2000-2002

- Efforts at several DOE sites involving various technologies
- Efforts not coordinated
- Early attempt at comparing efforts was First Symposium on Be Particulates and Their Detection
  - February 2002, Santa Fe, NM
  - Sponsored by DOE Network of Senior Scientists and Engineers and Los Alamos National Lab

Early Efforts (2)

- Laser Induced Breakdown Spectroscopy (LIBS)
  - Direct-solids technique
  - Pros
    - No liquid waste
    - One unit has air and wipe models
  - Cons
    - Not validated at multiple labs or field sites
    - Issues with precision at low $\mu g/m^3$ range
    - One unit requires cart
  - Not being actively pursued

Early Efforts (3)

- Microwave Induced Plasma Spectroscopy (MIPS)
  - Developed at Los Alamos National Lab in 2000
  - Has since been commercialized
  - Issues with precision at low $\mu g/m^3$ range
  - Additional validation work needed
  - Not being actively pursued

Early Efforts (4)

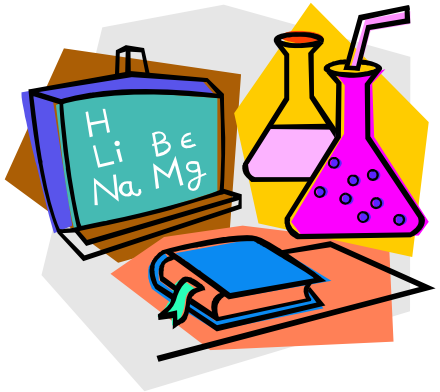
- Anodic Stripping Voltammetry
  - ELS Technology
  - Beryllium-specific
  - Portable
  - Generates liquid waste
  - Needs additional validation
  - Vendor interest has waned due to perceived low demand

Early Efforts (5)

- Time of Flight Mass Spectroscopy (TOFMS)
  - Transportable, not portable
  - Precision at low μg/m^3 range not well demonstrated
  - May be closer than LIBS, MIPS, or ASV; still some interest
  - Costly

Early Efforts (6)

- Others presented at February 2002 Symposium
  - Aerosol-Focusing LIBS (Oak Ridge/Y-12)
  - Surface-Enhanced Raman Scattering (Oak Ridge/Y-12)
  - Amzil Beryllium Air Monitor (no longer in business?)
  - Colorimetric wipes (LANL)
- Issues common to all:
  - Incomplete validation
  - Standard method not established/published (needed for AIHA accreditation purposes)
- Bottom line: un-coordinated efforts did not produce needed outcome



Be Advanced Technology Assessment Team

- NSSE established Beryllium Advanced Technology Assessment Team (BeATAT) after February 2002 symposium
- Key outputs of BeATAT:
  - Assessment Report
  - Draft Criteria for “Real-Time” Equipment
- Final report: June 2003

BeATAT Report

- Criteria development
  - Draft criteria completed December 2002
  - Separate criteria for air monitoring equipment and surface wipe analysis equipment
- Key Elements of Criteria
  - Terminology
  - Minimum Technical and Operational Specifications
    - Functionalities
    - Requirements
  - Technical Evaluation Criteria
  - Field Evaluation Criteria
- Focus on field-deployable, but not necessarily direct-reading, instrumentation

BeATAT Report – Selected Functionalities

- Common Functionalities
  - Reporting range of 0.05-5.0 μg/m^3 (air) or μg/wipe
    - Measurement uncertainty within ±25% throughout range
    - *This range may no longer be adequate given ACGIH proposed TLV*
  - Calibration
    - Covers full reporting range
    - Little or no disassembly required
  - Quality Control
  - Battery operation or backup
  - Data downloading

BeATAT Report – Selected Functionalities (2)

- Functionalities for Air Monitoring Equipment
  - User-selectable air sampling rate of 10-50 cfm
  - Aerodynamic particle sizing capabilities
    - Particle number, surface area, mass per m^3
    - Important to mimic size-selective inhalation characteristics
  - Digital alarm with selectable setpoint (range TBD)
  - Report results in $\mu g/m^3$
- Functionalities for Surface Wipe Equipment
  - Report results in $\mu g/100cm^2$

Efforts Since 2002

- Berylliant Fluorescence Analyzer
  - Specific for Be
  - Lab-Validated
  - Accepted by AIHA for accredited beryllium analysis
  - Not direct-reading or real-time
  - Generates liquid waste
- Second Symposium on Beryllium Particulates and Their Detection (2005)
  - Aerosol TOFMS (Y-12)
  - Raman spectroscopy (ORNL/Y-12)
  - Colorimetric wipe improvements

Efforts Since 2002 (2)

- Beryllium Health Research Agenda
  - Originated by NNSA Defense Programs in 2006
  - Ambitious agenda:
    - Real-time monitoring for both aerosols and surface samples
    - High-volume personal air pumps
  - Funding provided only in FY06, not subsequent years
  - No further progress expected

What We Need to Go Forward

- Technology
  - We have not really tried to find a DRI technology that would work for Be
  - Technologies like XRF will not work for Be due to its transparency to X-Rays
  - Thus, some technology development required
  - Technology for aerosols and for surfaces may or may not be the same
- Funding
  - Single-source approach to obtaining funding no longer viable
  - Multi-year effort needed to develop and deploy viable technology

What Will Drive Further Progress?

- Beryllium needs to be seen as more than a DOE issue
  - NAS study for Air Force may help
- Benefits for a real-time device (such as DRI) need to be more widely understood
  - Improved worker protection
  - Significant cost savings
  - Process improvements
- Collaboration on funding is needed
  - Multiple groups/sources kicking in for joint projects

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